



A study on solutions of poly (vinylpyrrolidone) in binary mixtures of DMSO+H₂O at different temperatures by ultrasonic velocity measurements

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Abstract – The ultrasonic velocities and densities of solutions of poly (vinylpyrrolidone) i.e. (PVP) (Mol. wt. \approx 40,000) have been measured in water and its binary mixtures with dimethylsulphoxide (DMSO) containing DMSO at 25 mol % intervals at 25°C, 35°C and 45°C. From velocity and density values, various acoustical parameters such as acoustical impedance (Z), adiabatic compressibility (β), intermolecular free length (l_f), relative association (R_A), molar sound velocity (R), Wada's constant (W), solvation number (S_n) and apparent molar adiabatic compressibility (ϕ_{κ}) have been evaluated. All these parameters have been discussed separately in terms of polymer-polymer and polymer-solvent interactions as a function of solvent composition and temperature.

Keywords – Ultrasonic velocity, density, poly(vinylpyrrolidone), dimethylsulphoxide (DMSO)

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1. Introduction

PVP is a water-soluble polymer and has large number of applications in industry, medicine and research *etc* [1,2]. Because of its diverse applications, considerable attention has been paid by the researchers in the study of interactions between macromolecules, solvent system and salts through various techniques, namely, ultrasonic velocity and viscosity *etc*. Some studies have been performed on polymer solutions by several investigators using ultrasonic velocity measurements in recent years [3,4] in order to understand polymer-solvent and polymer-polymer interactions and also structure of polymers. Therefore, in this communication, ultrasonic velocity and density measurements of solutions of poly (vinylpyrrolidone) in binary aqueous mixtures of dimethylsulphoxide have been reported over whole solvent composition range at 25°C, 35°C and 45°C. The various acoustical parameters thus derived from above data, have been discussed in terms of polymer-polymer and polymer-solvent interactions.

2. Experimental

The solvents, water and dimethyl sulfoxide (DMSO) have been

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purified as reported earlier [5]. Polymer poly vinylpyrrolidone i.e. (C₆H₉NO)_n (Extrapure, Sisco Research Laboratories Pvt. Ltd. Bombay) has been used as such, after drying for few hours. The solutions were prepared by adding a known weight of polymer to a fixed volume of solvent/solvent mixture and then stirring until a clear solution was obtained. The low concentration range (0% to 0.6%) has been studied in the solutions because of its high viscous nature.

Ultrasonic velocity (U) was measured at 1MHz using interferometer supplied by Mittal Enterprises, New Delhi which is a direct and simple device for measuring sound velocity in liquids.

A detailed procedure for the measurement of ultrasonic velocity and density (ρ) is described elsewhere [6]. The accuracy of both density and ultrasonic velocity measurements was estimated to be $\pm 0.002\%$ and $\pm 0.05\%$, respectively.

3. Results and discussion

The various measured and derived acoustical parameters of poly (vinylpyrrolidone) presented in Tables 1-5, have been calculated using the equations given in the literature [7-10]. The ultrasonic

Table 1. Wt%age (v/v), ultrasonic velocity (U), density (ρ), adiabatic compressibility (β), specific acoustic impedance (Z), Inter molecular free length (L_f), relative association (R_A), molar sound velocity (R), Wada's constant (W), solvation number (S_n) and apparent molar adiabatic compressibility (ϕ_{κ}) of PVP in 100 % H_2O at different temperatures.

Temperature	v/v%	$\rho \times 10^3$ Kg m ⁻³	U m s ⁻¹	$\beta \times 10^{10}$ m ² N ⁻¹	$Z \times 10^6$ Kg m ² s ⁻¹	$L_f \times 10^{11}$ m	$R \times 10^2$ m ^{10/3} s ^{-1/3}	$W \times 10^{11/7}$ m ^{19/7} N ^{1/7}	$S_n \times 10^2$	$\phi_{\kappa} \times 10$ m ³ s ² kg ⁻¹
25°C	0.0	0.9970	1500.0	4.4578	1.4955	4.3426	20.66	14.58	---	178.85
	0.1	0.9971	1502.6	4.4420	1.4980	4.3349	20.67	14.59	78.68	178.03
	0.2	0.9973	1503.4	4.4363	1.4993	4.3322	20.67	14.59	53.48	177.82
	0.3	0.9975	1504.4	4.4296	1.5006	4.3289	20.67	14.59	46.72	177.52
	0.4	0.9977	1505.6	4.4216	1.5021	4.3250	20.67	14.59	44.94	177.15
	0.5	0.9979	1506.3	4.4166	1.5031	4.3225	20.67	14.59	40.87	176.93
	0.6	0.9981	1507.2	4.4105	1.5043	4.3195	20.67	14.59	39.06	176.66
35 °C	0.0	0.9941	1525.4	4.3232	1.5161	4.3545	20.84	14.69	---	173.95
	0.1	0.9942	1527.3	4.3120	1.5184	4.3489	20.85	14.69	57.51	173.36
	0.2	0.9944	1529.4	4.2993	1.5208	4.3425	20.85	14.69	61.30	172.81
	0.3	0.9946	1530.8	4.2906	1.5225	4.3381	20.85	14.69	55.68	172.44
	0.4	0.9948	1533.2	4.2763	1.5252	4.3309	20.86	14.70	60.03	171.85
	0.5	0.9950	1535.0	4.2654	1.5273	4.3254	20.86	14.71	59.12	171.35
	0.6	0.9953	1537.2	4.2519	1.5300	4.3185	20.87	14.71	60.72	170.78
45°C	0.0	0.9902	1551.7	4.1943	1.5365	4.3660	21.05	14.81	---	169.4
	0.1	0.9904	1553.4	4.1843	1.5385	4.3607	21.05	14.81	52.93	168.88
	0.2	0.9905	1554.8	4.1763	1.5400	4.3566	21.05	14.82	47.58	168.56
	0.3	0.9907	1556.4	4.1669	1.5419	4.3517	21.05	14.82	48.25	168.14
	0.4	0.9908	1558.0	4.1579	1.5437	4.3470	21.06	14.82	48.02	167.76
	0.5	0.9910	1559.6	4.1486	1.5456	4.3421	21.06	14.82	48.18	167.35
	0.6	0.9912	1561.0	4.1403	1.5473	4.3378	21.06	14.83	47.39	166.98

velocity varies linearly with the increase in concentration of polymer in water, DMSO and all the studied mixtures. However, the velocity change is no more linear with the change in solvent composition as DMSO is added to water. In pure solvents, the velocity value shows a maximum at about 20-30 mol % and nearly 25 mol % DMSO Figure 1, which is in agreement as reported earlier [5]. Such a maximum has also been observed in other aquo-organic mixtures like methanol + water and ethanol + water [11]. This nonlinear behaviour of velocity with solvent composition has been attributed to the existence of solvent – solvent interactions, which are maximized nearer to 25 mol % of DMSO, which has been further supported by spectroscopic and other studies[11]. The purpose of this study is to observe the behaviour of velocity in these binary aqueous solvent mixtures after adding polymer as solute. It is clear from the Tables (1-5) that the magnitude of velocity increases with the addition of polymer but the velocity behavior remains the same as in the pure solvent mixtures. This clearly indicates that the solute-solvent interactions though present, hardly break the solvent-solvent interactions already present in the binary solvent mixtures. The same is true for maltose and fructose carbohydrates

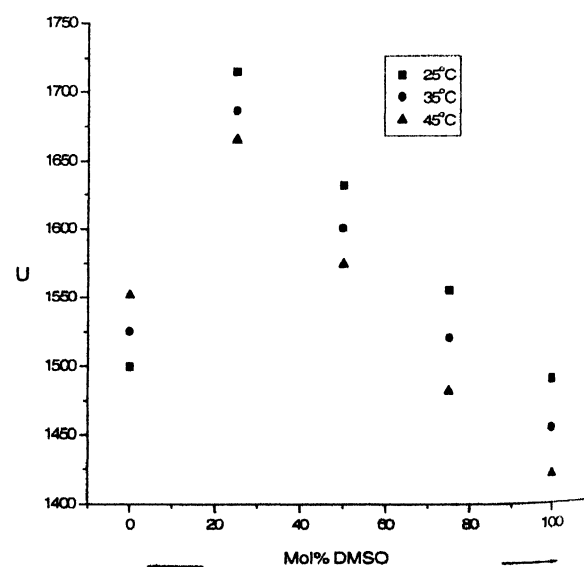


Figure 1. Plot of ultrasonic velocity (U) versus mol% DMSO in DMSO + H_2O solvent system of PVP at different temperatures.

Table 2. Wt% age (v/v), ultrasonic velocity (U), density (ρ), adiabatic compressibility (β), specific acoustic impedance (Z), Inter molecular free length (L_f), relative association (R_A), molar sound velocity (R), Wada's constant (W), solvation number (S_n) and apparent molar adiabatic compressibility (ϕ_{λ}) of PVP in 25 mol % DMSO at different temperatures

Temperature	v/v%	$\rho \times 10^{-3}$ Kg m ⁻³	U	$\beta \times 10^{10}$ m ² N ⁻¹	$Z \times 10^{-6}$ Kg m ⁻² s ⁻¹	$L_f \times 10^{11}$ m	$R \times 10^2$	$W \times 10^{11/7}$ m ^{19/7} N ^{1/7}	$S \times 10^{-2}$	$\phi_{\lambda} \times 10^{10}$ m ² s ² kg ⁻¹
35 °C	0.0	1.0808	1714.9	3.1461	1.8534	3.6481	24.68	17.51	---	116.44
	0.1	1.0816	1716.2	3.1390	1.8562	3.6440	24.67	17.50	40.46	115.97
	0.2	1.0818	1717.0	3.1384	1.8574	3.6437	24.67	17.50	30.17	115.87
	0.3	1.0821	1718.6	3.1288	1.8597	3.6382	24.67	17.50	32.79	115.59
	0.4	1.0824	1719.6	3.1243	1.8613	3.6356	24.66	17.50	30.96	115.39
	0.5	1.0827	1720.5	3.1202	1.8628	3.6332	24.66	17.50	29.40	115.22
	0.6	1.0829	1721.3	3.1167	1.8640	3.6311	24.66	17.50	27.78	115.07
	0.0	1.0740	1686.4	3.2740	1.8111	3.7895	24.70	17.52	---	121.94
	0.1	1.0741	1688.3	3.2663	1.8134	3.7850	24.71	17.52	42.16	121.56
	0.2	1.0742	1690.3	3.2583	1.8157	3.7804	24.72	17.53	42.94	121.25
	0.3	1.0743	1692.0	3.2514	1.8177	3.7764	24.72	17.53	41.17	121.06
	0.4	1.0745	1694.1	3.2428	1.8203	3.7714	24.73	17.53	42.58	120.64
45 °C	0.5	1.0746	1695.5	3.2371	1.8220	3.7681	24.73	17.54	40.25	120.42
	0.6	1.0747	1697.3	3.2299	1.8241	3.7639	24.74	17.54	40.05	120.15
	0.0	1.0656	1665.2	3.3843	1.7744	3.9217	24.79	17.57	---	127.04
	0.1	1.0657	1665.9	3.3812	1.7753	3.9199	24.79	17.57	15.33	126.87
	0.2	1.0658	1666.5	3.3784	1.7762	3.9183	24.79	17.57	14.15	126.76
	0.3	1.0659	1667.1	3.3756	1.7769	3.9167	24.79	17.57	14.53	126.65
	0.4	1.0661	1667.8	3.3722	1.7780	3.9147	24.79	17.57	14.59	126.50
	0.5	1.0662	1668.4	3.3695	1.7788	3.9132	24.79	17.57	14.25	126.37
	0.6	1.0663	1669.0	3.3667	1.7796	3.9115	24.79	17.57	14.48	126.26

taken as solutes in binary aqueous DMSO mixtures at all concentrations [5]. The variation of velocity with concentration is similar at all temperatures.

The adiabatic compressibility (β) values of polymer solution also vary nonlinearly with the change in solvent composition giving a minimum at about same composition range i.e. around 25 mol % DMSO indicating that solvent-solvent interactions are maximum in the same region of almost 25 mol % DMSO [5]. In Ref. [5], the ultrasonic velocity shows maximum at 30 mol% of DMSO, (given in Figure 1 as well as Table 1). The β -values decrease with increase in concentration of polymer. The decrease in β -values is due to the influence of solute on the surrounding solvent molecules leading to increase in internal pressure and thus the solution becomes harder to compress. The increase in internal pressure with the increase of concentration of polymer has been obtained in this case and this supports the above argument. Similar observations for the decrease of β has been reported in the literature of Shah and Parsania[4] for poly (4,4'-cyclohexylidene-2,2'-dimethyldiphenylene/diphenylene-3,3'-benzophenone

disulphonates) in chlorinated and aprotic solvents. Since polymer chains assume a variety of conformational changes under different experimental conditions like concentration, temperature, dielectric constant of the medium etc., the polymer may assume a coiled configuration in concentrated solutions and unfold to a greater extent on dilution in polar solvents which results in increase of viscosity. Since flexible polymers are more compressible due to chain like structure which is further supported by the decrease in isentropic compressibility (coiling up of polymer chain) with increasing concentration[4]. Such reduction in compressibility has been found in solutions of cellulose derivatives and polymer solutions of polystyrene in toluene[12]. With the increase in temperature, since adiabatic compressibilities increase, it clearly indicates temperature dependence of β . The value of intermolecular free length L_f shows a decreasing trend, which is in agreement with the observation made by Syal and coworkers[13] in case of ultrasonic studies of alkali bromides in DMSO + dioxane solvent system at 25°C. With increase in temperature, the magnitude of L_f increases, and is in good agreement with the theoretical

Table 3. Wt% age (v/v), ultrasonic velocity (U), density (ρ), adiabatic compressibility (β), specific acoustic impedance (Z), Inter molecular free length (L_f), relative association (R_f), molar sound velocity (R), Wada's constant (W), solvation number (S_n) and apparent molar adiabatic compressibility (ϕ_{λ}) of PVP in 50 mol % DMSO at different temperatures

Temperature	v/v%	$\rho \times 10^{-3}$ Kg m ⁻³	U m s ⁻¹	$\beta \times 10^{10}$ m ² N ⁻¹	$Z \times 10^{-6}$ Kg m ⁻² s ⁻¹	$L_f \times 10^{11}$ m	$R \times 10^2$ m ^{10/3} s ^{-1/3}	$W \times 10^{11/7}$ m ^{19/7} N ^{1/7}	$S_n \times 10^{-2}$	$\phi_{\lambda} \times 10$ m ⁴ s ⁻² Kg ⁻¹
25°C	0.0	1.0986	1632.0	3.4176	1.7929	3.8023	31.35	22.35	---	124.43
	0.1	1.0988	1632.5	3.4149	1.7938	3.8009	31.35	22.34	10.78	124.28
	0.2	1.0989	1634.0	3.4083	1.7956	3.7972	31.36	22.35	18.56	124.02
	0.3	1.0991	1635.4	3.4018	1.7975	3.7936	31.36	22.35	21.00	123.75
	0.4	1.0993	1636.4	3.3971	1.7989	3.7909	31.36	22.35	20.42	123.55
	0.5	1.0994	1638.0	3.3901	1.8008	3.7870	31.37	22.35	21.89	123.20
	0.6	1.0995	1638.3	3.3886	1.8013	3.7864	31.37	22.35	19.22	123.23
35 °C	0.0	1.0894	1600.5	3.5834	1.7436	3.9645	31.42	22.38	---	131.57
	0.1	1.0895	1601.7	3.5778	1.7451	3.9614	31.42	22.38	21.34	131.29
	0.2	1.0896	1602.9	3.5721	1.7465	3.9582	31.43	22.38	21.51	131.07
	0.3	1.0897	1604.2	3.5660	1.7481	3.9548	31.43	22.39	22.06	130.87
	0.4	1.0898	1605.0	3.5621	1.7491	3.9527	31.43	22.39	20.23	130.69
	0.5	1.0899	1606.6	3.5547	1.7510	3.9486	31.44	22.39	21.78	130.40
	0.6	1.0990	1607.2	3.5226	1.7663	3.9307	31.44	22.39	21.34	128.67
45°C	0.0	1.0801	1574.6	3.7342	1.7007	4.1195	31.52	22.44	---	138.29
	0.1	1.0802	1575.1	3.7315	1.7014	4.1180	31.52	22.44	19.97	138.11
	0.2	1.0803	1575.6	3.7287	1.7021	4.1164	31.52	22.44	19.95	138.01
	0.3	1.0804	1576.2	3.7255	1.7029	4.1147	31.52	22.44	19.52	137.90
	0.4	1.0805	1576.9	3.7228	1.7036	4.1132	31.52	22.44	17.84	137.79
	0.5	1.0806	1577.2	3.7202	1.7043	4.1117	31.52	22.44	18.65	137.68
	0.6	1.0808	1577.8	3.7166	1.7053	4.1098	31.52	22.44	19.12	137.32

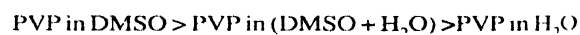
requirements and the literature data. However, the behaviour of β and L_f in water and various water + DMSO mixtures gives minimum for β and L_f nearer to 25 mol % DMSO.

The value of Z shows gradual increase with the increase of concentration of polymer in water and other mixtures. This is in agreement with the theoretical requirement because U and ρ both increase with the increase of concentration. However, the Z -values show maximum in the same region of 20-30 mol % and nearer to 25mol %DMSO. Increase of Z , with concentration of polymer has also been reported by Sanariya and Parsania [14].

The decrease of β , and increase of U and Z with increasing concentrations in a particular system, is indicative of strong polymer – solvent interaction. This is further supported by non-linear increase of R and decrease of L_f with concentration [4].

It has been found that molar sound velocity (R) and molar adiabatic compressibility represented as Wada's constant (W) are independent of temperature, pressure and concentration, which is in accordance with the R and W -values for unassociated and weakly associated molecules [6]. However, R and W -values are found to increase as DMSO content is increased in the

solvent mixture *i.e.*, R and W values of PVP in these systems are in the following order:



which is supported by the 2: 1 complex formation of H₂O with DMSO mixture as given earlier[11]. Similar observations have been obtained for PEG in DMSO+H₂O system by Srilalitha and coworkers[8]. Higher values of R and W in H₂O + DMSO systems have been obtained as compared to the PVP in H₂O, similar to that reported by Srilalitha and coworkers[8]. In the present study, H₂O+DMSO solvent system may also have 2:1 complex formation and interaction between this complex and PVP may be responsible for the higher ultrasonic velocities and R -values of PVP in H₂O. +DMSO solvent system compared to other system *i.e.* PVP in H₂O. The higher values of R in DMSO in comparison to its value in H₂O may be accounted for the non-formation of hydrogen bonding in PVP-DMSO system whereas there may be molecular association by hydrogen bonding of PVP with water. This may be possible at the oxygen sites in PVP in H₂O) and H₂O+DMSO system. Similar results have been reported by Srilalitha and coworkers[8] for PEG inDMSO+H₂O solvent system. Similar temperature invariance of Rao's number and

Table 4. Wt% age (v/v), ultrasonic velocity (U), density (ρ), adiabatic compressibility (β), specific acoustic impedance (Z), Inter molecular free length (L_f), relative association (R_r), molar sound velocity (R), Wada's constant (W), solvation number (S_n) and apparent molar adiabatic compressibility (ϕ_{λ}) of PVP in 75 mol % DMSO at different temperatures.

Temperature	v/v%	$\rho \times 10^{-3}$ Kg m ⁻³	U m s ⁻¹	$\beta \times 10^{10}$ m ² N ⁻¹	$Z \times 10^{-6}$ Kg m ⁻² s ⁻¹	$L_f \times 10^{11}$ m	$R \times 10^3$ m ^{10/3} s ^{-1/3}	$W \times 10^{11/7}$ m ^{19/7} N ^{1/7}	$S_n \times 10^{-2}$	$\phi_{\lambda} \times 10^{10}$ m ⁴ s ⁻² kg ⁻¹
25°C	0.0	1.0977	1556.0	3.7627	1.7080	3.9897	44.94	32.09		137.11
	0.1	1.0979	1556.5	3.7596	1.7088	3.9881	44.94	32.09	7.73	136.93
	0.2	1.0981	1557.2	3.7555	1.7100	3.9859	44.94	32.09	8.97	136.76
	0.3	1.0983	1558.4	3.7490	1.7116	3.9825	44.94	32.09	11.36	136.49
	0.4	1.0985	1559.2	3.7445	1.7128	3.9801	44.94	32.09	11.32	136.30
	0.5	1.0986	1560.2	3.7394	1.7140	3.9774	44.95	32.10	11.57	136.10
	0.6	1.0988	1561.0	3.7349	1.7152	3.9750	44.95	32.09	11.57	135.91
35°C	0.0	1.0885	1521.0	3.9711	1.6556	4.1735	44.98	32.12		145.93
	0.1	1.0886	1522.2	3.9645	1.6571	4.1700	44.98	32.13	15.59	145.61
	0.2	1.0887	1523.6	3.9569	1.6587	4.1660	44.99	32.13	16.76	145.31
	0.3	1.0888	1525.0	3.9492	1.6604	4.1620	45.00	32.14	17.22	145.02
	0.4	1.0889	1526.4	3.9416	1.6621	4.1579	45.01	32.14	17.37	144.72
	0.5	1.0890	1527.4	3.9361	1.6633	4.1550	45.02	32.15	16.47	144.51
	0.6	1.0891	1528.6	3.9296	1.6648	4.1516	45.03	32.15	16.26	144.25
45°C	0.0	1.0782	1482.8	4.2182	1.5987	4.3783	45.03	32.15		156.49
	0.1	1.0783	1483.4	4.2144	1.5995	4.3764	45.03	32.15	13.91	156.29
	0.2	1.0784	1483.9	4.2112	1.6002	4.3747	45.03	32.15	11.62	156.17
	0.3	1.0785	1484.4	4.2080	1.6015	4.3730	45.03	32.15	12.70	156.03
	0.4	1.0786	1484.9	4.2047	1.6016	4.3713	45.03	32.15	12.41	155.90
	0.5	1.0787	1485.5	4.2010	1.6024	4.3694	45.03	32.15	12.84	155.74
	0.6	1.0788	1486.0	4.1977	1.6031	4.3677	45.03	32.15	12.24	155.61

Wada's constant have been noticed in DMSO+H₂O system by other workers[8] in case of polymer solution of aqueous and non-aqueous liquids.

It is clear from Tables (1-5) that the S_n values vary linearly with concentration in H₂O and pure DMSO. However in mixtures, it varies nonlinearly with concentration in DMSO + H₂O mixtures. Further, it has been found that the S_n -values are larger in H₂O at all concentrations than that in pure DMSO, which is due to the two lone pairs of electrons available for the interaction in case of H₂O. Thus, the structures of the polymers, polymer – solvent and polymer – polymer interactions are influenced more profoundly in solvents of different polarity as reported by Shah and Parsania [4]. At higher temperatures, S_n -values vary nonlinearly with concentration for all the mixtures studied. Similar type of behaviour has also been reported by Rakkapan and Punitha[12] in case of ultrasonic studies of ethyl cellulose in alcohols. Ultrasonic velocity study of chloroform and dichloroethane solutions of cardopolysulfone of 1,1'-bis (3-methyl-4-hydroxy-phenyl) cyclohexane and 4,4'-difluorodiphenyl sulfone by Kamani and Parsania [15] reveals

that there occur strong polymer solvent interactions and is supported by positive value of solvation number (S_n). S_n -values show almost negligible variation with concentration.

The calculated values of ϕ_{λ} of PVP have been presented in Tables (1-5) in DMSO, H₂O and all the studied mixtures. From the tables, it is clear that ϕ_{λ} -values show a gradual decrease with increase in solute concentration in all the studied mixtures (water + DMSO) including pure solvents.

This type of behaviour is similar to that as reported by Syal *et al* [16] for tetra alkylammonium salts in AN+ dioxane systems. The apparent molar adiabatic compressibility (ϕ_{λ}) has been plotted (Figure 2) for PVP in water + DMSO mixtures against square root of concentration *ie* ϕ_{λ} vs \sqrt{C} . ϕ_{λ} and S_n have been evaluated from these plots at different temperatures in accordance with the least square computer program and has been reported in Table 6.

The calculated values of ϕ_{λ} presented in Table 6 for PVP in DMSO + H₂O at different temperatures are all positive indicating the presence of solute-solvent interactions.

Table 5. wt% age (w/v), ultrasonic velocity (U), density (ρ), adiabatic compressibility (β), specific acoustic impedance (Z), inter molecular length (L_f), relative association (R_f), molar sound velocity (R), Wada's constant (W), solvation number (S_n) and apparent molar adiabatic compressibility (ϕ_{AS}) of PVP in 100 mol % DMSO different temperatures.

Temperature	w/v%	$\rho \times 10^3$ Kg m ⁻³	U m s ⁻¹	$\beta \times 10^{10}$ m ² N ⁻¹	$Z \times 10^6$ Kg m ⁻² s ⁻¹	$L_f \times 10^{11}$ m	$R \times 10^2$ m ^{10/3} s ^{-1/3}	$W \times 10^{11/7}$ m ^{19/7} N ^{1/7}	$S_n \times 10^{-2}$	$\phi_{\text{AS}} \times 10$ m ³ s ⁻² kg
25°C	0.0	1.0954	1490.9	4.1071	1.6331	4.1683	81.48	58.29	---	149.97
	0.1	1.0955	1493.8	4.0907	1.6364	4.1600	81.53	58.32	20.42	149.21
	0.2	1.0956	1494.6	4.0860	1.6374	4.1576	81.53	58.33	13.12	149.07
	0.3	1.0957	1495.6	4.0802	1.6387	4.1546	81.54	58.33	11.14	148.86
	0.4	1.0959	1496.8	4.0729	1.6403	4.1509	81.55	58.34	10.62	148.5
	0.5	1.0961	1497.8	4.0667	1.6417	4.1478	81.55	58.34	10.02	148.37
	0.6	1.0962	1498.8	4.0609	1.6430	4.1448	81.56	58.35	9.54	148.11
35 °C	0.0	1.0854	1454.1	4.3573	1.5783	4.3717	81.55	58.34	---	160.58
	0.1	1.0856	1455.4	4.3488	1.5800	4.3674	81.55	58.34	9.97	160.18
	0.2	1.0858	1456.2	4.3432	1.5811	4.3646	81.55	58.34	8.26	159.9
	0.3	1.0859	1457.5	4.3350	1.5827	4.3605	81.57	58.35	8.71	159.61
	0.4	1.0860	1458.8	4.3269	1.5843	4.3564	81.59	58.36	8.89	159.26
	0.5	1.0861	1459.7	4.3212	1.5854	4.3535	81.60	58.37	8.44	159.1
	0.6	1.0862	1461.0	4.3131	1.5869	4.3495	81.62	58.37	8.60	158.76
45°C	0.0	1.0751	1420.7	4.6084	1.5274	4.5764	81.69	58.43	---	171.46
	0.1	1.0753	1422.0	4.5991	1.5291	4.5718	81.71	58.43	10.32	170.92
	0.2	1.0755	1422.8	4.5931	1.5302	4.5688	81.71	58.43	8.48	170.75
	0.3	1.0756	1425.0	4.5785	1.5327	4.5615	81.74	58.45	11.04	170.16
	0.4	1.0757	1426.4	4.5691	1.5344	4.5568	81.75	58.46	10.87	169.80
	0.5	1.0759	1428.0	4.5580	1.5364	4.5513	81.77	58.47	11.14	169.36
	0.6	1.0760	1430.0	4.5448	1.5387	4.5447	81.81	58.49	11.71	168.85

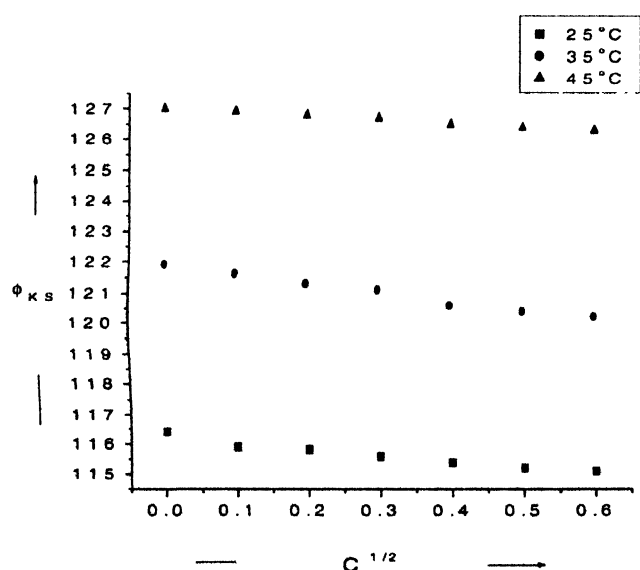


Figure 2. Plot of apparent molar adiabatic compressibility (ϕ_{AS}) versus $C^{1/2}$ of PVP in 25 mol% DMSO at different temperatures.

Table 6. Limiting apparent molar adiabatic compressibility (ϕ_{AS}^0) slope S_K for PVP in water, DMSO and DMSO + H₂O mixtures different temperatures.

Mol % DMSO	25 °C		35 °C		45 °C	
	$\phi_{\text{AS}}^0 \times 10^{10}$	$S_K \times 10^{10}$	$\phi_{\text{AS}}^0 \times 10^{10}$	$S_K \times 10^{10}$	$\phi_{\text{AS}}^0 \times 10^{10}$	$S_K \times 10^{10}$
0.0	179.10	-3.05	175.29	-5.61	170.34	-4
25.0	116.70	-2.07	122.62	-3.11	127.34	-1
50.0	125.06	-2.42	133.46	-5.37	138.61	-1
75.0	137.71	-2.27	146.61	-2.98	156.81	-1
100.0	150.11	-2.47	161.19	-3.00	172.66	-4

In pure solvent system, ϕ_{AS} values decrease with increase DMSO content up to 25 mol % DMSO in DMSO + H₂O mixture and then increase with the further increase of DMSO in DM + H₂O mixtures. Also, with the increase of temperatures, the values increase slightly in magnitude.

Conclusions

From the above observations, it can be concluded that solut

solvent interactions are present in this system, maximized at the same region where solvent-solvent interactions happen to be at their maximum. Furthermore, polymer acts as structure maker in binary mixtures of water and DMSO over the whole solvent composition range.

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